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Japanese Patent Application Unexamined Publication No. 49-42600

Publication Date: April 22, 1974

Japanese Patent Application No. 47-86427

Filing Date: August 29, 1972

### Application

1. TITLE OF THE INVENTION

METHOD FOR PRODUCING TUNGSTEN CARBIDE POWDER

2. INVENTORS

Akio HARA et al.

3. PATENT APPLICANT

Sumitomo Electric Industries, Ltd.

4. REPRESENTATIVE

Attorney, Hidemi AOKI

5. LIST OF ATTACHED DOCUMENTS

Specification one copy

Drawings one copy

Power of Attorney one copy

Duplicate of petition one copy

### SPECIFICATION

1. TITLE OF THE INVENTION

METHOD FOR PRODUCING TUNGSTEN CARBIDE POWDER

2. CLAIMS

A method for producing a tungsten carbide powder, which

comprises mixing a carbon powder in an amount of 3 to 4 equivalents based on the  $\text{WO}_3$  content in ammonium paratungstate ( $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ) or tungstic acid ( $\text{H}_2\text{WO}_4$ ), heating the mixture to a temperature of  $800^\circ\text{C}$  or lower in an inert gas atmosphere such as  $\text{N}_2$ , Ar gas or the like or in vacuum, then heating it to a temperature of  $1000^\circ\text{C}$  or higher in the atmosphere described above so as to control the oxygen concentration to 0.5% or less, and further heating it to a temperature of 1400 to  $2000^\circ\text{C}$  in  $\text{H}_2$  atmosphere.

### 3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a method for producing WC under a stable condition directly from ammonium paratungstate or from tungstic acid.

With the method of producing WC powder that is currently employed commonly in the industry,  $\text{WO}_3$  obtained by heating tungstic acid ( $\text{H}_2\text{WO}_4$ ) or ammonium paratungstate crystal ( $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ) is reduced in  $\text{H}_2$  atmosphere, or either tungstic acid crystal or ammonium paratungstate crystal is reduced directly in  $\text{H}_2$  atmosphere so as to obtain a metal W powder to which carbon is added and heated to a temperature of 1400 to  $2000^\circ\text{C}$  so as to undergo carbonizing reaction and produce WC powder.

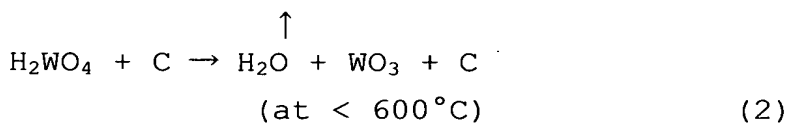
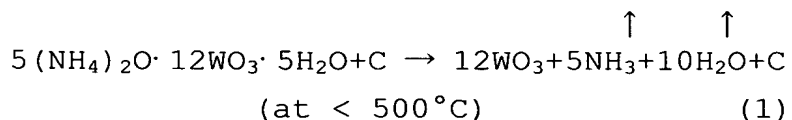
The method of producing WC directly from ammonium paratungstate or tungstic acid, in contrast, can not only shorten the process but also do away with intermediate processes such as mixing and continuously produce WC, thus offering many advantages including the capability of preventing the purity from

decreasing.

The reason why it has not been possible in the prior art to produce WC directly from ammonium paratungstate or tungsten oxide is that it has been difficult to control the carbon content and WC powder that is obtained has incomplete crystallinity and uneven particle size distribution that make the WC powder not suitable as the material to make cemented carbide.

The present inventors have made a basic research to provide an industrial method that solves the problems described above.

At temperatures not higher than 500°C, ammonium paratungstate reacts as shown in the scheme ① and tungstic acid reacts as shown in the scheme ②.

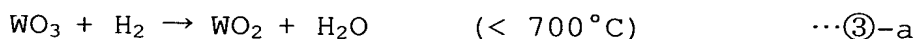


At temperatures higher than that described above, it is considered that reaction between  $\text{WO}_3$  and C becomes dominant. Therefore, the present inventors have made a basic research on the reaction of  $\text{WO}_3 + \text{C}$ , and closely investigated the causes of variation in the carbon content and abnormal particles to occur.

Now the reaction in which WC is generated directly from  $\text{WO}_3$

will be described below.

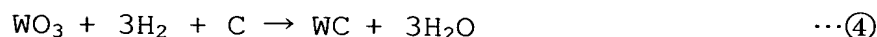
It is common to mix  $\text{WO}_3$  and carbon powder and cause the mixture to react in a stream of hydrogen in a Tamman furnace. It is generally believed that this reaction proceeds as shown in the scheme:  $\text{WO}_3 + 3\text{C} + \text{H}_2 \rightarrow \text{WC} + 3\text{CO} + \text{H}_2\text{O} \cdots \textcircled{3}$ . However, it was found from the research conducted by the present inventors, that this reaction can be divided into the following four reactions:



The reaction ( $\textcircled{3}\text{-c}$ ) is the so-called aqueous reaction, and it is a known fact that this reaction is sensitive to and is influenced by the temperature, a flow rate of  $\text{H}_2$  and other factors. It was also found that this reaction makes it difficult to control the carbon content. Fig. 1 shows the change in carbon content during the reaction of  $\text{WO}_3$  and  $3\text{C}$ . This shows an example of a case where the powder layer is 50 mm thick and  $\text{H}_2$  is supplied in a small quantity. This graph shows that carbon content does not change and stable production of W is observed also with X ray till the temperature reaches  $1000^\circ\text{C}$ . As the temperature becomes higher, reaction ( $\textcircled{3}\text{-c}$ ) is initiated and the carbon content decreases.

As local distribution of the reactions is shown in Fig. 2, sufficient quantity of  $\text{H}_2$  is supplied and  $\text{H}_2\text{O}$  produced in the

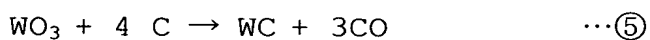
reaction is satisfactorily dispersed in the portion near the surface, and consequently the reaction (③-c) hardly occurs. The reaction in such a case proceeds as shown in the scheme ④.



As a result, in principle, WC including stable carbon content is produced when such a process is implemented as a small powder is caused to fully react with  $\text{H}_2$  such that the reaction (③-c) does not occur. To apply this process to industrial production, it is desirable to control the thickness of the powder layer to remain small and supply a sufficient flow of  $\text{H}_2$  gas so as to keep sufficient dispersion of the produced gas. On the industrial scale of the reaction, on the other hand, it is necessary to have a large quantity of material to react in a short period of time. Thus such problems newly arise as the reaction (③-c) becomes dominant and/or water generated in the reaction reacts with the heat generating object thereby leading to shortened life time of the furnace. On the other hand, it has been known to have metal powder react with C in vacuum or an inert gas atmosphere without using  $\text{H}_2$  gas. However, there have been such problems such as  $1700^\circ\text{C}$  or higher temperature is required for complete production of WC with such a method, and particles have pores or abnormal crystal formed inside thereof, though the amount of carbon bonded in the produced WC is near the theoretical value.

In consideration of such problems, the present inventors

paid attention to the fact that the generation of  $H_2O$  that causes the problems described above does not occur when  $WO_3$  is reduced by carbon only, without using  $H_2$ . If  $H_2$  is not involved in the carbonizing reaction, however, it is difficult to obtain normal WC that has bonded carbon content near the theoretical value. Accordingly, the present inventors reduced the material in an inert gas atmosphere and then carbonized the metal in  $H_2$  gas stream, thus succeeding in the production of normal WC. This process is represented by the following schemes.



In other words, the process comprises the first step of reduction of the scheme  $\textcircled{5-a}$  that proceeds at a temperature from 1000 to 1600°C, and the second step of carbonizing reaction represented by the scheme  $\textcircled{5-b}$  that proceeds at a temperature from 1400 to 2000°C in  $H_2$  atmosphere.

It was found that the problem related to the reaction of  $WO_3$  and C can be easily solved by controlling the carbon content, particle size and particle size distribution by the method described above.

Furthermore, through a trial production of WC directly from  $WO_3$  on the industrial basis, it was found that the  $WO_3+4C$  mixture included near 2% of water content.

Fig. 3 shows the dehydration process. In Fig. 3, the graph

① shows the amount of water (weight percentage) removed from the  $\text{WO}_3+\text{C}$  mixture in 15 minutes at each temperature when heated in  $\text{N}_2$  stream. The graph shows that dehydration of  $\text{WO}_3+4\text{C}$  occurs at a low temperature of  $100^\circ\text{C}$  and at a high temperature of  $300^\circ\text{C}$  or higher. The water content cannot be removed from the  $\text{WO}_3+4\text{C}$  mixture by heating at  $150^\circ\text{C}$  (② in Fig. 3). It was found that water content that is removed at high temperatures can be completely removed by heating at  $600^\circ\text{C}$  (③ in Fig. 3). Even when the first step of the carbonizing reaction is carried out in  $\text{N}_2$  atmosphere so that  $\text{H}_2\text{O}$  will not be generated, water contained in the  $\text{WO}_3+4\text{C}$  mixture is released in the furnace thereby having significant influence on the carbon content and particle size distribution in the carbide when a large quantity of metal is carbonized on the industrial basis. Such water remaining in the furnace may cause damage on the furnace.

It is very difficult to completely remove water content from the raw material of  $\text{WO}_3$  and carbon powder so as to eliminate the possibility of adsorption of water when mixing the powders in a process of industrial scale production.

Therefore, when WC is produced directly from a large quantity of  $\text{WO}_3$ , it is necessary to carry out dehydration in  $\text{N}_2$  atmosphere at a temperature of  $800^\circ\text{C}$  or lower, before the first stage of reduction in  $\text{N}_2$  atmosphere at a temperature from 1000 to  $1600^\circ\text{C}$ .

Through investigation on the process of direct



carbonization of  $\text{WO}_3$  on the industrial basis described above, it was found that the process becomes exactly the same as that of a case where  $\text{WO}_3$  is used as the raw material represented by the scheme ① and the scheme ② since heating at a temperature of  $600^\circ\text{C}$  or lower is necessary regardless of whether the starting material is ammonium paratungstate ( $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ) or tungstic acid ( $\text{H}_2\text{WO}_4$ ), as long as the process of dehydration is required.

That is, WC can be produced based on similar concept to that of direct carbonization of  $\text{WO}_3$ , by carefully mixing ammonium paratungstate or tungstic acid crystal and a predetermined quantity of carbon powder, heating the mixture to a temperature of  $800^\circ\text{C}$  or lower to dehydrate in  $\text{N}_2$  atmosphere, carrying out the first stage of carbonization in  $\text{H}_2$  atmosphere at a temperature of  $1000^\circ\text{C}$  or higher and carrying out the second stage of carbonization in  $\text{H}_2$  atmosphere at a temperature from 1400 to  $2000^\circ\text{C}$ .

In this case, the WC powder having a carbon content near the theoretical value can be obtained through the reactions represented by the schemes (⑤-a) and (⑤-b), by mixing 4 equivalents of a carbon powder to the  $\text{WO}_3$  that remains after the heat treatment at  $800^\circ\text{C}$  or lower.

According to the present invention, raising the temperature to higher than  $800^\circ\text{C}$  in the first stage causes the removed water and carbon to react thus leading to variation in the quantity of carbon. When the secondary carbonizing reaction that is the

second stage of reduction is carried out in inert atmosphere at a temperature not higher than  $1000^{\circ}\text{C}$ , the reaction of the scheme (④-a) does not proceed satisfactorily with  $\text{O}_2$  left remaining after the secondary carbonizing reaction.  $\text{O}_2$  reacts with  $\text{H}_2$  in the secondary carbonizing reaction to produce  $\text{H}_2\text{O}$  thus causing variation in the quantity of carbon.

When the secondary carbonizing reaction is carried out at a temperature higher than  $1600^{\circ}\text{C}$ , crystal grains start to grow before complete WC is generated, resulting in the production of WC having abnormal crystal.

When the tertiary carbonization that is the third stage of carbonizing reaction is carried out in inert atmosphere at a temperature of  $1400^{\circ}\text{C}$  or lower, bonded carbon content does not reach the value dictated by stoichiometry. At temperatures of  $2000^{\circ}\text{C}$  and higher, WC that has been produced decomposes so as to produce  $\text{W}_2\text{C}$  again, which is useless as the material to produce cemented carbide.

The present invention is intended to produce WC on the industrial basis, and is characterized by the three-stage carbonizing process that realizes a commercially practical process in a field where production process of industrial scale could not be provided because of direct reaction of the material was caused to proceed in  $\text{H}_2$  atmosphere or in vacuum in the prior art. Specifically, it is preferable to control the production process so that the material to be reacted makes sufficient

contact with the gas in order to satisfactorily disperse the gas generated in the reaction and supply carbon in the form of  $\text{CH}_4$  gas in the tertiary carbonizing reaction. Therefore, a complete WC powder that can be used in the industry is obtained by having the reaction proceed in a reaction furnace that stirs the powder during reaction or in a rotary carbonizing furnace wherein the metal is carbonized while rotating.

Since it is the prerequisite of the present invention to carry out the reaction in three stages, a rotary carbonizing furnace described in Japanese Patent Application No. Sho 46-71233 is configured in three stages wherein the first stage is set at a temperature from 400 to 800°C in  $\text{N}_2$  atmosphere, the second stage is set at a temperature from 1000 to 1600°C in  $\text{N}_2$  atmosphere, and the third stage is set at a temperature from 1600 to 2000°C in  $\text{H}_2$  atmosphere with the material supplied from the top of the furnace to flow continuously, which makes it possible to easily produce WC.

#### Example 1

0.33 Equivalents of a carbon powder was added to  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$  crystal of 200  $\mu$ , and was sufficiently mixed in a ball mill for 10 hours. Water was added to the mixture and, after sufficiently kneading the mixture with a kneader, the material was extruded from an extruding machine to form granulated powder measuring about 2 mm in diameter and 2 mm in length.

The granulated powder was caused to react in a three-stage

rotary carbonizing furnace. Material was charged continuously to the furnace where the first stage was set at a temperature of 600°C in N<sub>2</sub> atmosphere, the second stage was set at a temperature of 1400°C in N<sub>2</sub> atmosphere and the third stage was set at a temperature of 1800°C in H<sub>2</sub> atmosphere. NH<sub>3</sub> and H<sub>2</sub>O generated in the first stage were passed together with N<sub>2</sub> gas through a water tank so as to be recovered as NH<sub>4</sub>OH.

The carbide thus obtained was 2  $\mu$  in size and WC was normal crystal, and was sufficiently applicable to practical use as the material to produce cemented carbide with total carbon content of 6.23% and free carbon content of 0.10%. This was mixed with 10% of a Cu powder and the mixture was sintered at 1400°C for one hour to obtain an alloy. This showed exactly the same characteristics as the WC obtained by a carbonizing metal W powder.

#### Comparative Example 1

0.4 Equivalents of carbon powder was added to 5 (NH<sub>4</sub>)<sub>2</sub>O · 12WO<sub>3</sub> · 5H<sub>2</sub>O crystal of 200  $\mu$ , and was sufficiently mixed in a ball mill. Then the mixture was encased in a carbon case and put into a Tamman furnace so as to react in H<sub>2</sub> stream at 1800°C. This resulted in abnormal WC that was coagulated including T.C 1.43 and F.C 0.00.

#### Comparative Example 2

0.7 Equivalents of carbon powder was added to 5 (NH<sub>4</sub>)<sub>2</sub>O · 12WO<sub>3</sub> · 5H<sub>2</sub>O and the mixture was caused to react under the conditions described above, resulting incomplete WC with T.C 7.30 and F.C

5.31.

Example 2

0.35 Equivalents of carbon powder was added to  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$  crystal of  $100 \mu$ , and was mixed in a ball mill. Water was added to the mixture that was then kneaded for about two hours. The material was extruded from an extruding machine to form a granulated powder.

The granulated powder was subjected to reduced pressure drying at  $600^\circ\text{C}$  in a vacuum drier for three hours and was caused to react in a rotary carbonizing furnace of two-stage construction where the first stage was set at a temperature of  $1300^\circ\text{C}$  in  $\text{N}_2$  atmosphere and the second stage was set at a temperature of  $1600^\circ\text{C}$  in  $\text{H}_2$  atmosphere. The carbide thus obtained had a particle size of  $1 \mu$  and showed T.C 6.27% and F.C 0.17%. This carbide had a very uniform particle size distribution and was sufficiently applicable to practical use as the material WC for cemented carbide.

Example 3

3 Equivalents of carbon powder was added to a  $\text{H}_2\text{WO}_4$  powder and was sufficiently mixed by using a ball mill. Water was added to the mixture and, after kneading the mixture, the material was extruded from an extruding machine to form a granulated powder.

The  $\text{H}_2\text{WO}_4 + \text{C}$  mixture was heated at  $700^\circ\text{C}$  in  $\text{N}_2$  gas stream and was then subjected to first carbonization at  $1200^\circ\text{C}$  in  $\text{N}_2$  stream and the second carbonization at  $1800^\circ\text{C}$  in  $\text{H}_2$  stream in the rotary

carbonizing furnace.

The carbide thus obtained had a particle size of 2  $\mu$  and showed T.C 6.28% and F.C 0.14%. This carbide was mixed with 7% of a Co powder and was processed in an acetone solution using a ball mill for 100 hours. After drying, the mixed powder was press-molded at 1425°C for one hour.

The alloy thus obtained had characteristics as follows.

Physical properties	Specific gravity	Hardness (HR <sub>A</sub> )	Breakage strength
Value	14.90	91.3	230 kg/mm <sup>2</sup>

The alloy also had very homogeneous structure, and the WC powder was sufficiently applicable to practical use as the material for cemented carbide.

All of the examples described above used a mixture of ammonium paratungstate or tungstic acid and carbon powder as the starting material. However, required quantity of carbide can be produced by mixing a required quantity of carbon powder even when ammonium paratungstate and tungstic acid coexist, or oxide of tantalum, molybdenum or the like or a material that can produce such an oxide is mixed. In other words, the present invention can be embodied by making modifications such as adding other additives to an extent that does not compromise the object and effects of the present invention.

#### 4. BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the changes in carbon content when  $\text{WO}_3+3\text{C}$  is reacted in  $\text{H}_2$ , Fig. 2 shows a model of  $\text{WO}_3+\text{C}$  reaction, and Fig. 3 shows the amount of  $\text{H}_2\text{O}$  (weight percentage) removed from the  $\text{WO}_3+4\text{C}$  mixture in 15 minutes when heated at each temperature.

<Fig. 1>

Carbonizing temperature and change in carbon content

Change in carbon content

Process temperature

<Fig. 2>

$\text{WO}_3-3\text{C}$  reaction model

Carbon boat

<Fig. 3>

Dehydration process of  $\text{WO}_3+\text{C}$  mixture

Quantity of water generated

Heating temperature

Dehydrated at  $150^\circ\text{C}$

Dehydrated at  $600^\circ\text{C}$

#### AMENDMENT

##### 1. INDICATION OF CASE

Japanese Patent No. 86427

##### 2. TITLE OF THE INVENTION

METHOD FOR PRODUCING TUNGSTEN CARBIDE POWDER

##### 3. PERSON WHO MAKES AMENDMENT

Sumitomo Electric Industries, Ltd.

Representative, Isamu SAKAMOTO

4. REPRESENTATIVE

Attorney, Hidemi AOKI et al.

5. DATE OF ORDER FOR AMENDMENT

Voluntary Amendment

6. OTHER INVENTORS, PATENT APPLICANTS OR REPRESENTATIVE

(1) Inventor

Masaya MIYAKE

(2) Patent applicant

(3) Representative

Attorney, Masashi YOSHITAKE

7. OBJECT FOR AMENDMENT

(1) Correct " $(5(\text{NH}_4)_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O})$ " in page 7, lines 11 to 12 of the specification to " $(5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O})$ ".

(2) Correct "characteristics (typographical error)" in page 10, line 13 of the specification to "characteristics".





(2,000円)

# 特 許 願 (1)

昭和47年 8 月 9 日

特許庁長官 三宅幸夫殿

## 1. 発明の名称

タングステンカーバイド粉末の製造法

## 2. 発明者

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(電話大阪 461-1031)  
氏 名 (7085) 弁理士 青 木 秀 実  
(ほか1名)

## 5. 添付書類の目録

- (1) 明細書 1 通
- (2) 図面 1 通
- (3) 委任状 1 通
- (4) 願書副本 1 通

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## 明 細 書

### 1. 発明の名称

タングステンカーバイド粉末の製造法

### 2. 特許請求の範囲

パラタングステンアンモニウム ( $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ) もしくはタングステン酸 ( $\text{H}_2\text{WO}_4$ ) に含有される  $\text{WO}_3$  量に対して 3~4 当量の炭素粉末を混合し、 $\text{H}_2$ 、 $\text{Ar}$  ガス等の不活性雰囲気中もしくは真空中にて  $800^\circ\text{C}$  以下の温度で加熱しこれをさらに上記雰囲気中で  $1000^\circ\text{C}$  以上の温度で加熱し酸素含有量を 0.5% 以下にした後、さらに  $\text{H}_2$  雰囲気中にて  $1400 \sim 2000^\circ\text{C}$  の温度で加熱することを特徴とするタングステンカーバイド粉末の製造法

### 3. 発明の詳細な説明

本発明はパラタングステン酸アンモニウム若しくはタングステン酸から直接 WC を安定して製造する方法に関するものである。

現在一般に工業的に採用されている WC 粉末の製造法はタングステン酸 [ $\text{H}_2\text{WO}_4$ ] もしくはパラタングステンアンモニウム結晶 [ $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ ] を加熱して  $\text{WO}_3$  とした後  $\text{H}_2$  中で還元す

## ① 日本国特許庁

# 公開特許公報

①特開昭 49-42600

④3公開日 昭49.(1974) 4.22

②特願昭 47-86427

②出願日 昭47(1972) 8.29

審査請求 未請求 (全5頁)

庁内整理番号

⑤2日本分類

7141 41  
6452 42  
6809 42  
7059 41

15 N22  
10 A61  
10 G52  
203C32

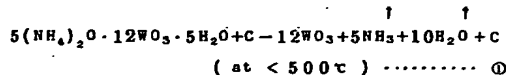
るかもしくは直接タングステン酸結晶パラタングステンアンモニウム結晶を  $\text{H}_2$  中で還元することにより得た金属 W 粉末に炭素を加え、 $1400 \sim 2000^\circ\text{C}$  にて炭化反応させ、WC 粉末を得ている。

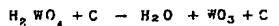
これに対してパラタングステンアンモニウムもしくはタングステン酸から直接 WC を得る方法は工程を短縮出来るばかりでなく途中の混合工程など省略でき、連続的に WC を生成させるため純度の低下を防ぐことが出来るなど数多くの利点がある。

従来タングステン酸、タングステンアンモニウムもしくは酸化タングステンから直接 WC を製造し得なかつた理由は炭素量の調整が困難であつたのと及び得られた WC 粉末の結晶が不完全であり粒度分布も不揃いであるため超硬合金原料として使用に適さなかつたことにある。

本発明者等は上記欠点を解消せる工業生産法を提供するため基礎研究を行なつた。

$500^\circ\text{C}$  以下ではタングステンアンモニウムは①式の如くタングステン酸は②式の如く反応する。





(at < 800°C) ..... ④

これ以上の温度では  $\text{WO}_3$  と  $\text{C}$  の反応になると考えられる。そこで  $\text{WO}_3 + \text{C}$  の反応について基礎的検討を行ない炭素量の変動及び異常粒子の発生原因について詳しく調べた。

次に  $\text{WO}_3$  から直接  $\text{WC}$  が生成される反応形態について説明する。

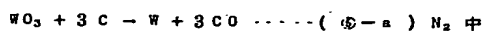
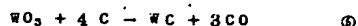
一般には  $\text{WO}_3$  と炭素粉末を混合し、タンマン炉の水素気流中で反応させられる。この反応式は  $\text{WO}_3 + 3\text{C} + \text{H}_2 \rightarrow \text{WC} + 3\text{CO} + \text{H}_2\text{O}$  ..... ⑤ であると一般に言われているが本発明者らの研究の結果この反応は次の4反応にわけて考えられることがわかった。



(⑤-c) 反応はいわゆる水性反応であり、これが温度及び  $\text{H}_2$  流量等によつて敏感に左右されることは周知の事実である。そしてこの反応が起るために炭素量の調節が難しいことが明らかと

を若しく縮めるといふ新たな問題も生じてくる。また  $\text{H}_2$  ガスを使用しないで真空中もしくは不活性ガス中で  $\text{C}$  と反応させることは知られている。しかしこれらの方法によれば完全な  $\text{WC}$  を作るためには  $1700^\circ\text{C}$  以上の温度が必要であり、また生成  $\text{WC}$  の結合炭素量はほぼ理論的に近いが粒子内部に孔があつたりして異常結晶が出来るという問題があつた。

本発明者らはこれらの事情を考へて、 $\text{WO}_3$  の還元を  $\text{H}_2$  を使用せず炭素のみで還元させれば上記障害の原因となる  $\text{H}_2\text{O}$  の発生がないことに着眼した。しかし  $\text{H}_2$  が炭化反応して関与しなければ最終的に理論値までの結合炭素量を持つ正常な  $\text{WC}$  が得難いので、還元過程を不活性雰囲気中で行い次に  $\text{H}_2$  気流中にて炭化せしむることにより正常な  $\text{WC}$  を得ることに成功した。反応式としては

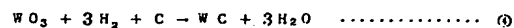


である。すなわち (⑥-a) 式の1段目還元を  $1000 \sim 1600^\circ\text{C}$  の間で行ない、(⑥-b) 式の2段目炭化反応を  $\text{H}_2$  中で  $1400^\circ\text{C} \sim 2000^\circ\text{C}$  の間で

特開昭49-42600 (2)

なつた。第1図は  $\text{WO}_3 + 3\text{C}$  の反応時におけるカーボン値の変動を示す。これは粉末層の厚みが  $50\text{mm}$  である場合であり  $\text{H}_2$  の供給が少ない場合の例である。これによれば  $1000^\circ\text{C}$  までは炭素量の変動がなく、X線的にも安定して  $\text{W}$  の生成が認められる。さらに高温になると (⑥-c) の反応が起り  $\text{C}$  値は減少する。

ところで部分的に見た反応形態は第2図に示すように表面層は  $\text{H}_2$  の供給が充分に多く、また反応して発生する  $\text{H}_2\text{O}$  の放散が充分に行なわれるため、(⑥-c) の反応はほとんど起らない。このような場合は⑥の反応式で反応が進む。



従つて原理的に考えると少量の粉末で  $\text{H}_2$  と充分反応させ (⑥-c) 反応が起らないようにすれば炭素量の安定した  $\text{WC}$  が生成される。これを工業的に生産するためには粉末層の厚みを薄くコントロールして  $\text{H}_2$  ガスを充分流し、発生するガスの放散をよくすることが望ましい。しかし一方工業的生産規模では短かい時間で大量に反応を進ませる必要がある。そのため (⑥-c) の反応が優先したり発生する水分が発熱体と反応して炉体寿命

行いものである。

$\text{WO}_3 + \text{C}$  の反応については炭素量の調整及び粒度、粒度分布の調整を上記方法において行えば容易に解決することがわかつた。

さらにこの考え方に従つて工業的に  $\text{WO}_3$  が直接  $\text{WC}$  を製造することを試みた結果  $\text{WO}_3 + 4\text{C}$  の混合物は2%近く水分を含むことがわかつた。

第3図にその脱水過程を示す。第3図グラフ①は  $\text{WO}_3 + \text{C}$  の混合物を  $\text{N}_2$  気流中各温度で15分間にわたる水分量 (wt%) である。これによると  $\text{WO}_3 + 4\text{C}$  に含まれる水分は  $100^\circ\text{C}$  の低温で出る水分と  $300^\circ\text{C}$  以上の高温で発生する水分がある。この  $\text{WO}_3 + 4\text{C}$  の混合物を  $150^\circ\text{C}$  で加熱してもこの水分はとれない。(第3図②)。 $600^\circ\text{C}$  で加熱処理すると高温で発生する水分は完全にとれることがわかつた (第3図③)。

1次炭化を  $\text{N}_2$  中で行つて  $\text{H}_2\text{O}$  の発生がないようにしても  $\text{WO}_3 + 4\text{C}$  混合物そのものが含有している水分が炉内で発生するため、工業ベースで大量の炭化を行う時は炭化物の炭素量、粒度分布に大きな影響を与える。またこれらの水分が炉内に溜りやすくと炉体損傷の原因ともなる。

原料  $W_2O_5$  及び炭素粉末の水分を完全になくし、またこれらの粉末を混合する時に水分の吸着が絶対にならないようにすることは工業的規模での生産では非常に困難である。

よつて大量に  $W_2O_5$  から直接 WC を製造する時は、 $H_2$  中 1000℃ ~ 1600℃ の 1 段還元をする前に、 $N_2$  中 800℃ 以下の温度で脱水処理を行う必要がある。

以上の工業ベースでの  $W_2O_5$  の直接炭化を検討した結果脱水処理工程を必要とすれば初期原料がパラタングステンアンモニウム ( $5(NH_4)_2O \cdot 12W_2O_5 \cdot 5H_2O$ ) であつてもタングステン酸 ( $H_2WO_4$ ) であつても 800℃ 以下で加熱処理が必要なので①式④式の如く  $W_2O_5$  を原料としたものと全く同じ工程となることがわかつた。

すなわちパラタングステンアンモニウム、もしくはタングステン酸結晶に所定量の炭素粉末を十分混合し、 $N_2$  中 800℃ 以下の温度で加熱脱水処理し、 $H_2$  中 1000℃ 以上の温度で 1 次炭化、 $H_2$  中 1400℃ ~ 2000℃ の温度で 2 次炭化を行うことにより、 $W_2O_5$  の直接炭化と同じような考え方で WC を得ることが出来る。

するもので、従来  $H_2$  中もしくは真空中で直接に反応させたため工業的規模の製造法に至らなかつたのを 3 段炭化法にて実用化したことを特徴としている。具体的製造法としては反応時に生成するガスの放散をよくし、また 3 次炭化でカーボンを  $CH_4$  として気体より供給するために充分気体と被反応物を接触させるように操作する方が望ましい。よつて反応時に粉末を攪拌する反応炉、もしくは回転しながら炭化する回転炭化炉にて反応させれば工業的に使用される完全な WC 粉末が得られる。

本発明の反応は 3 段階の条件があるため特願 46-71233 号で示されている回転炭化炉を 3 段に組み合わせ 1 段目を  $N_2$  雰囲気 400 ~ 800℃ とし、2 段目を  $N_2$  雰囲気 1000 ~ 1600℃、3 段目を  $H_2$  雰囲気 1800℃ ~ 2000℃ とし、炉の上部から連続的に流すことにより容易に WC を製造し得る。

#### 実施例 1.

200g の  $5(NH_4)_2O \cdot 12W_2O_5 \cdot 5H_2O$  結晶に、0.33 当量の炭素粉末を混ぜボールミルにて 10 時間十分に混合した。さらにこれらの混合物に水を加えニーダーで十分混練を行つた後押出機で押

特開 昭 49-42600 (3)

またこの時に必要となる炭素量は 800℃ 以下の加熱処理後に残る  $W_2O_5$  に対して 4 当量の炭素粉末を混合すれば (⑤-a) (⑤-b) 式に従つて反応が起り得られた WC 粉末は理論値に近い炭素量を持つものが得られる。

本発明において 1 段目の加熱温度を 800℃ 以上にあげると発生する水分と炭素が反応して炭素量の変動要因となる。また 2 段目の還元行程である 2 次炭化反応を不活性雰囲気中で 1000℃ 以下で行うと (⑤-a) 式の反応が充分に進まず、2 次炭化後でも  $O_2$  が残っている。この  $O_2$  は 2 次炭化において  $H_2$  と反応し、 $H_2O$  となつて炭素量の変動要因となる。

また 2 次炭化を 1600℃ 以上の温度で行うと完全な WC が生成される前に粒成長が起きるため、異常結晶を持つ WC が生成される。

また 3 段目の炭化反応である、3 次炭化を 1400℃ 以下の温度で行うと結合炭素が化学量論値に達しない。また 2000℃ 以上では生成した WC が分解して再び  $W_2C$  が生成されいづれも超硬合金の原料としては実用にならない。

本発明は工業的に WC を製造することを目的と

出して  $2 \sim 4 \times 2 \sim 4$  位の造粒粉とした。

この造粒粉末を 3 段からなる回転式炭化炉を用い、 $N_2$  雰囲気 600℃ とし、また 2 段目を  $N_2$  雰囲気 1400℃、3 段目を  $H_2$  雰囲気 1800℃ の条件として連続的に流した。1 段目で発生する  $NH_3$  及び  $H_2O$  は  $N_2$  ガスと共に水槽の中に通し  $NH_4OH$  として回収した。

得られた炭化物は 2g であり WC は正常結晶であつた。全炭素量 0.23% 遊離炭素量 0.10% で超硬合金原料として十分使用に適するものであつた。これを 10% の Cu 粉末と混合し 1400℃ × 1 Hr の条件で焼結した合金を得た。これは金属 W 粉末を炭化して得た WC と全く同じ特性であつた。

#### 比較例 2

200g の  $5(NH_4)_2O \cdot 12W_2O_5 \cdot 5H_2O$  に 0.4 当量の炭素粉末を加えボールミルで混合した後カーボンケースに装入し、横型タンマン炉で  $H_2$  気流中 1800℃ で反応を行なさせた。

その結果 T.C 1.43 P.C 0.00 の凝集した異常  $W_2C$  となつてしまつた。

#### 比較例 3

上記条件で  $5(NH_4)_2O \cdot 12W_2O_5 \cdot 5H_2O$  に 0.7

当量の炭素粉末を加えて反応を行なわせたが、T.C 73.0%、F.C 63.1%にて完全なWCとなり得なかつた。

#### 実施例2

100μの5(NH<sub>4</sub>)<sub>2</sub>O・12WO<sub>3</sub>・5H<sub>2</sub>O結晶に0.35当量の炭素粉末をボールミルにて混合し、さらに水を加えて混練機で2時間ほど練つた。

これを押出機を用いて造粒粉とした。

この造粒粉を真空乾燥機で600℃3時間減圧乾燥した。これを2段階造からなる回転式炭化炉で反応させた。1段目はN<sub>2</sub>雰囲気1300℃、2段目をH<sub>2</sub>雰囲気中で1600℃の条件で行つた。得られた炭化物は粒度1μであり、T.C 62.7%、F.C 0.17%であつた。この炭化物は粒度分布も非常に揃つていて超硬合金の原料WCとして十分使用に適するものであつた。

#### 実施例3

H<sub>2</sub>WO<sub>4</sub>粉末に3当量の炭素粉末をボールミルを用いて十分混合した。さらに水を用いて混練した後押出機にて押出して造粒粉とした。

このH<sub>2</sub>WO<sub>4</sub>+C混合物をN<sub>2</sub>気流中700℃で加熱した後回転炭化炉を用いてN<sub>2</sub>中1200℃で1次炭

化を行ない、H<sub>2</sub>中1800℃にて2次炭化を行つた。

得られた炭化物は2μであり、T.C 62.8%、F.C 0.14%であつた。この炭化物に7%のCo粉末を加えアセトン溶媒中で100時間ボールミルした。乾燥後この混合粉末を型押しして1425℃×1hrにて焼結した。

得られた合金の特性は下記の様であつた。

	比 重	硬度 (HR <sub>c</sub> )	抗 折 力
特 性 値	14.90	91.3	230 kg/mm <sup>2</sup>

組織も非常に均一であり、このWC粉末は超硬合金原料として十分使用されるものであつた。

尚以上の実施例においてはどれもパラタングステンアンモニウムまたはタングステン酸と炭素粉末を混合したものを出発材料とするものについて示したが、必要によつてはパラタングステンアンモニウムと、タングステン酸が混在しても、またタンタル、モリブデン等酸化物乃至酸化物生成機能を有するものが混在していても所要量の炭素粉末を配合することによつて所要の炭化物を得ることが出来る。即ち本発明の実施に当つては、本発

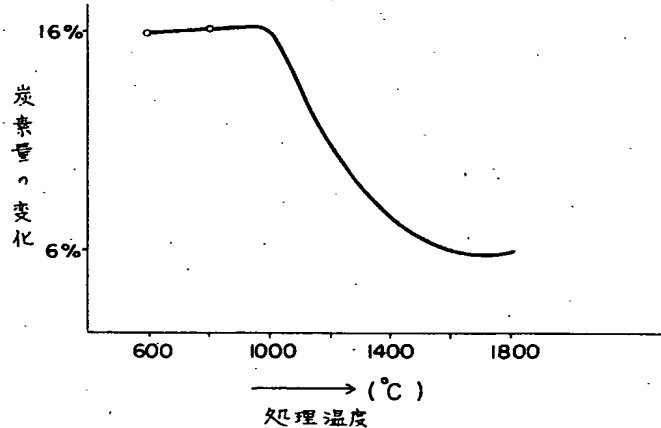
明の目的、効果を損なわない範囲で他の添加物を加える等附加変更を加えることが出来るものである。

#### 4. 図面の簡単な説明

第1図はWO<sub>3</sub>+3CをH<sub>2</sub>中で反応させた時のカーボン値の変動を示す図表、第2図はWO<sub>3</sub>+Cの反応モデル図、第3図はWO<sub>3</sub>+4C混合粉末を各温度1.5分間加熱した時に発生するH<sub>2</sub>O量(重量%)を示すものである。

代理人 弁理士 青木秀実  
代理人 弁理士 吉竹昌司

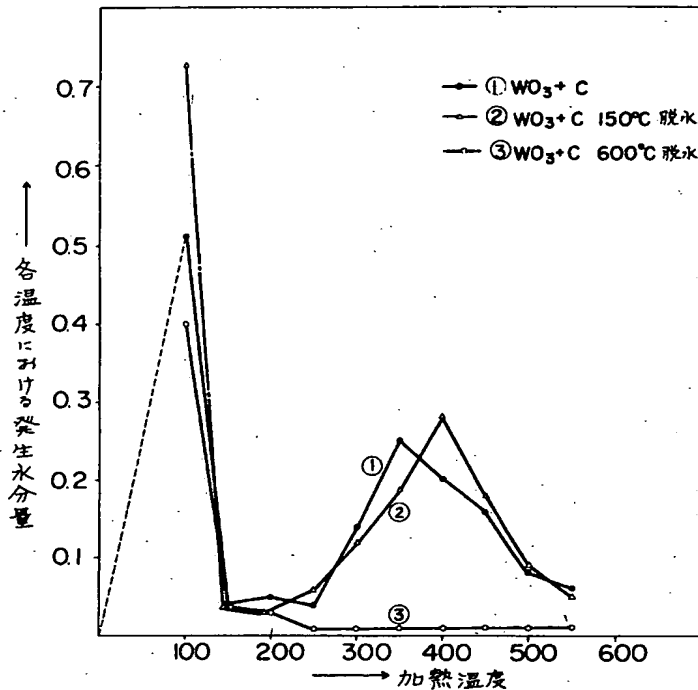
第1図 炭化温度と炭素の変動  
WO<sub>3</sub>-3C



第2図 WO<sub>3</sub>-3C 反応形態図

5min	WO <sub>3</sub> +3H <sub>2</sub> +C → WC+3H <sub>2</sub> O
10min	WO <sub>3</sub> +2H <sub>2</sub> +2C → WC+2H <sub>2</sub> O+CO
50min	WO <sub>3</sub> +H <sub>2</sub> +3C → WC+3CO+H <sub>2</sub> O

カーボンポット

才3図 WO<sub>3</sub> + C 混合物の脱水分過程

## 手続補正書

昭和47年10月5日

特許庁長官 三宅幸夫 殿

## 1. 事件の表示

特 許  
昭和47年実用新案登録願第80427号

## 2. 発明考案の名称

タングステンカーバイド粉末の製造法

## 3. 補正をする者

事件との関係 特許出願人  
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氏 名 (5936) 弁理士 吉竹 昌司

## 5. 補正命令の日付

昭和 年 月 日

自発補正

## 6. 前記以外の発明者、特許出願人または代理人

## (1) 発 明 者

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## 6. 補正の対象

明細書中、発明の詳細な説明の欄

## 7. 補正の内容

①明細書第7頁第11～12行目

「 $(5(\text{NH}_4)_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O})$ 」を「 $(5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O})$ 」に訂正する。

②明細書第10頁第13行目

「特性」を「特性1」に訂正する。

# LA CERAMICA

organo ufficiale della federceramica

CON LA COLLABORAZIONE DELL'ENTE NAZIONALE DELLA CERAMICA E DEI SILICATI E DEL CENTRO CERAMICO DELL'UNIVERSITA' DI BOLOGNA

ANNO XXXIII

Gennaio-Febbraio 1980

NUMERO 1

## Preparazioni di polveri ultrafini di carburo di tungsteno

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### RIASSUNTO

L'impiego del Carburo di Tungsteno e degli altri carburi ha avuto in questo ultimo decennio un incremento notevole sia nel campo degli utensili che nel campo delle alte temperature. Le prestazioni che i componenti in carburo di Tungsteno forniscono trattandosi di materiale sinterizzato, dipendono principalmente dalle loro caratteristiche strutturali e in ultima analisi dalla qualità delle polveri di partenza (omogeneità, granulometria ecc.). La relazione ha lo scopo di riportare il lavoro svolto per uno studio applicativo di processi di preparazione di polveri ultrafini per la sintesi del Carburo di Tungsteno. In particolare l'attività svolta si è articolata nelle seguenti fasi:

- Preparazione di polveri ultrafini di anidride tungstica/grafite per liofilizzazione o atomizzazione della miscela Metatungstato di ammonio/grafite colloidale.
- Sintesi del Carburo di Tungsteno per riduzione carbo-termica della miscela preparata.
- Caratterizzazione prodotto finale.

### SUMMARY

*During these last years the use of Tungsten Carbide and other carbides has been increased both in tools application and in the field of high temperatures.*

*The performance of sintered Tungsten Carbide components, derives principally from their structural characteristics and as consequence from the starting powders quality.*

*The purpose of this work regards the study of preparing process of ultrafine powders for Tungsten Carbide synthesis. The phases of the experimental work have been the following:*

- *Preparation of ultrafine powders of Tungsten oxide/graphite through freeze-drying or spray-drying of colloidal mixture of ammonium of meta-tungstate/graphite.*
- *Synthesis of tungsten carbide through carbothermal reduction of the mixture.*
- *Final product characterization.*

### INTRODUZIONE

L'importanza del Carburo di Tungsteno nella moderna tecnologia non ha bisogno di presentazioni. Ricordiamo solo, in generale, che esso è il principale costituente delle leghe dure refrattarie sinterizzate.

Queste leghe, scoperte nel 1923 e messe in commercio a partire dal 1930 dalle Officine Krupp, sono ineguagliabili per molteplici usi taglio - lavoro al tornio e lavorazione a macchina dei materiali più duri (acciai, ghise, bronzi, porcellane, vetro, plastiche); industria mineraria; pezzi diversi per lavori di grande fatica. La loro estrema durezza limita l'usura degli utensili e dei pezzi, il che assicura una regolarità di calibraggio, irrealizzabile con l'ac-

ciaio da taglio rapido (1).

L'impiego del Carburo di Tungsteno e degli altri carburi, ha avuto in quest'ultimo decennio un incremento notevole, in quanto lo sviluppo tecnologico ha richiesto, e quindi permesso di sfruttare non solo le loro proprietà di durezza e di resistenza ad usura, ma anche la loro resistenza nel campo delle alte temperature.

L'ampliamento quindi del campo di applicazione di questi materiali ha portato ad un notevole incremento degli studi sulla loro fabbricazione, con l'applicazione di tecniche e processi sempre più sofisticati, ma comunque atti ad ottenere prodotti con caratteristiche ottimali.

Sia che l'applicazione avvenga nel campo degli utensili, sia che avvenga nel campo delle alte temperature, il par-

ticolare in carburo fornisce prestazioni che dipendono principalmente dalle sue caratteristiche strutturali. Infatti, trattandosi di sinterizzati, la loro qualità è tanto migliore quanto più elevata è la loro densità e quanto più omogenea e fine è la loro granulometria.

Partendo da questo presupposto si è voluto sviluppare uno studio applicativo di processi di preparazione di polveri ultrafini per la fabbricazione del Carburo di Tungsteno.

## 1. PROCESSI DI FABBRICAZIONE DEL CARBURO DI TUNGSTENO

La fabbricazione del Carburo di Tungsteno avviene nella maggior parte dei casi partendo da minerali o composti di W e trasformandoli in  $WO_3$ .

Successivamente si effettua una riduzione in forno a W metallico e si conclude il processo con il trattamento di carburazione in atmosfera riducente (2 - 3)

Tale processo, però, richiede più fasi successive, che lo rendono relativamente complesso e lungo.

Una semplificazione può avvenire introducendo, nella fase di preparazione, tecniche di disidratazione e di essiccamento dei prodotti di partenza, che recentemente hanno avuto larga applicazione nel campo dei materiali ceramici e refrattari: l'atomizzazione e la liofilizzazione (4 - 5 - 6 - 7).

Inoltre si può facilitare e rendere più rapido il processo effettuando un unico trattamento di riduzione, detto "Carbotermica", della miscela anidride tungstica-carbonio (3 - 7).

Nel corso del lavoro di seguito descritto sono stati esaminati i prodotti parziali e finali ottenuti introducendo queste tecniche di fabbricazione, con un accurato controllo delle caratteristiche chimico-fisiche del Carburo di Tungsteno ottenuto.

## 2. PARTE SPERIMENTALE

### 2.1 Ottenimento miscela $WO_3/C$

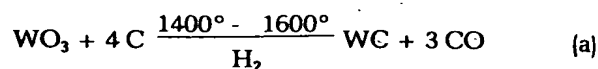
L'approccio iniziale del procedimento è quello di realizzare la miscelazione  $WO_3 + C$  già nella prima fase del processo.

SOSTANZA	PRODOTTORE	STATO FISICO	FORMULA	CONCENTRAZIONE g/l	DENSITA' g/cm <sup>3</sup>	pH
METATUNGSTATO DI AMMONIO	H. STANKE	SOLUZIONE	$[(NH_4)_2O]_3 \cdot 12 WO_3 \cdot 52 H_2O$	535 ( $WO_3$ )	1,48	3-4
ACQUADAG	ACHESON	SOSPENSIONE COLLOIDALE	C GRAFITICO	201,05 (C)	1,1	10,5

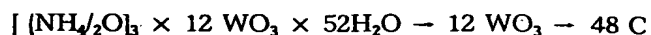
Tab. 1 - Caratteristiche chimico-fisiche dei prodotti di partenza per la fabbricazione del carburo di tungsteno

A questo scopo sono stati scelti come prodotti di partenza una soluzione di metatungstato di ammonio ed una sospensione di grafite colloidale, le cui caratteristiche di partenza sono rappresentate nella tab. 1. Queste sostanze sono state mescolate in proporzione di 48 parti di grafite per ogni parte di metatungstato di ammonio, poichè dalla

reazione generale [3]:



la proporzione stechiometrica Metatungstato/grafite è data da:



### 2.2 Essiccazione

La miscela così ottenuta è stata suddivisa ed essiccata mediante due differenti metodi:

- a) Liofilizzazione
- b) Atomizzazione.

Inoltre, per confronto, una terza parte è stata essiccata mediante evaporazione dell'acqua e dell'ammonio in stufa a 150°C.

#### a) Liofilizzazione

Il processo di liofilizzazione della miscela soluzione metatungstato di ammonio/sospensione grafite colloidale è stato condotto impiegando i parametri riportati in tab. 2.

LIOFILIZZAZIONE		ATOMIZZAZIONE	
CONDIZIONI DI CONGELAMENTO	IMMERSIONE IN AZOTO LIQUIDO		
ISOFORMA DI CONGELAMENTO	-25°C	VELOCITA' ROTAZIONE TURBINA	30'000 GIRI/MIN.
TEMPERATURA SUBLIMAZIONE	-30°C	TEMPERATURA DI ESSICCAMENTO	350°C
SBALZO TERMICO	-55°C	TEMPERATURA USCITA ARIA	120°C
TEMPO DI SUBLIMAZIONE	6 ORE	ALIMENTAZIONE	1 l/h
VUOTO	1-10 <sup>-3</sup> TORR.		

Tab. 2 - Parametri di essiccazione della miscela metatungstato di ammonio/grafite

La scelta dei parametri, in relazione ai principi pratici della liofilizzazione, è subordinata anche alle caratteristiche tecniche ed ai limiti dell'apparecchio usato. Il rapido raffreddamento mediante iniezione in  $N_2$  liquido della soluzione favorisce il mantenimento nella massa congelata della medesima concentrazione che si ha in fase liquida. In relazione ai limiti di cui sopra del nostro apparecchio la temperatura di sublimazione di + 30°C realizza, con la temperatura di congelamento di - 25°C, uno sbalzo termico di 55°C che assicura un rapido (6 ore) ed efficace essiccamento del prodotto (il vuoto sale infatti a 1.10<sup>-3</sup> Torr.).

I parametri soprariportati sono emersi da precedenti esperienze condotte con sbalzi termici minori che non portavano il processo a completamento (fase di sublimazione) ma s'arrestavano alla fusione.

Il prodotto ottenuto si presenta come una polvere molto fine, ma soprattutto molto omogenea nella dimensione

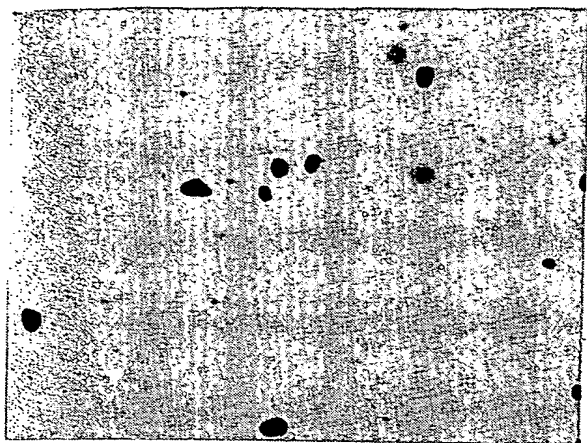
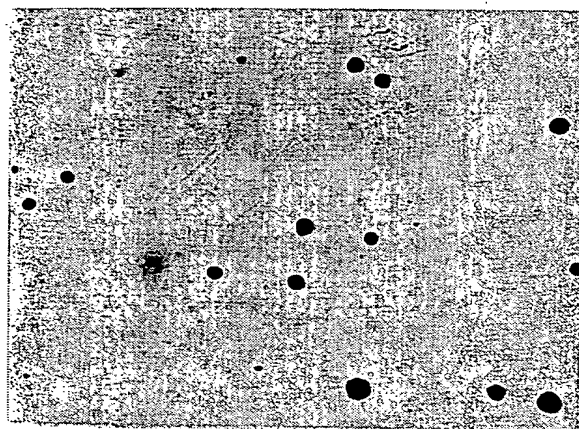
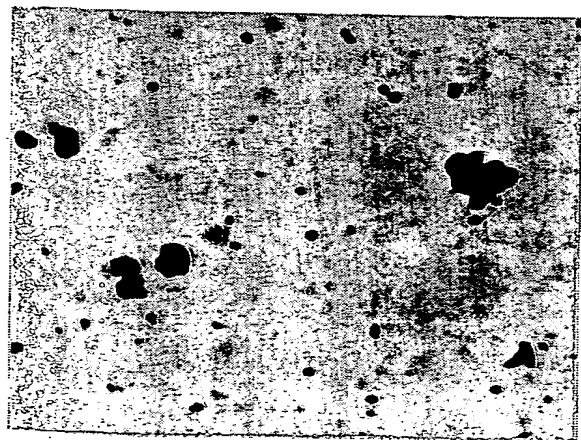
a)  $\bar{\phi} = 10 \mu$ b)  $\bar{\phi} = 10 \mu$ c)  $\bar{\phi} = 30 \mu$ 

Fig. 1 - Aspetto delle miscele di polveri Metatungstato Grafite dopo essiccamento per: a) Liofilizzazione b) Atomizzazione c) Evaporazione (200 X)

granulometrica che è mediamente di  $10 \mu$ . (La fig. 1a rappresenta l'aspetto della polvere dopo essiccamento per liofilizzazione).

La miscelazione risulta essere molto intima e non si os-

servano sedimentazioni né di grafite, né di metatungstato di ammonio.

#### b) Atomizzazione

Il processo è stato ottimizzato riguardo al sistema metatungstato di ammonio/grafite al fine di ottenere le seguenti caratteristiche delle polveri:

- forma dei granuli sferoidale
- dimensione dei granuli, la più piccola possibile
- essiccamento il più rapido possibile.

ESSICCAMENTO	TEMP. TRATTAMENTO	COMPOSTI PRESENTI			
		WC	W <sub>2</sub> C	W	GRAFITICO
LIQFILIZZATO	1400°C	PRESENTE	TRACCE	ASSENTE	PRESENTE
"	1500°C	"	"	"	"
"	1600°C	"	ASSENTE	TRACCE	ASSENTE
ATOMIZZATO	1400°C	"	TRACCE	ASSENTE	PRESENTE
"	1500°C	"	"	"	"
"	1600°C	"	ASSENTE	"	TRACCE
EVAPORATO	1400°C	"	PRESENTE	"	PRESENTE
"	1500°C	"	"	"	"
"	1600°C	"	TRACCE	"	"

Tab. 3 - Fasi e composti presenti nelle polveri di Carburo di Tungsteno rilevati mediante diffrazione RX.

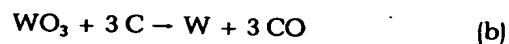
Le condizioni ottimali risultanti sono riportate in tab. 2. Infatti, come evidenziato dalla fig. 1b, si ottiene una polvere a granulometria molto fine ( $\bar{\phi} = 10 \mu$ ) analoga alla polvere liofilizzata, ma con una spiccata forma sferoidale. L'aspetto, infine, della polvere essiccata in stufa a 150°C, presenta notevole disomogeneità nella forma e soprattutto nella dimensione dei granuli ( $\bar{\phi} = 30 \mu$ ; fig. 1c). Riassumendo quindi si può affermare che sia la liofilizzazione che l'atomizzazione sono processi in grado di dare una polvere a granulometria molto fine ed omogenea, ma soprattutto permettono di realizzare una intimità di miscelazione irrealizzabile con altri processi di essiccamento.

Inoltre l'atomizzazione è in grado di produrre una polvere con caratteristiche di sfericità che la rendono più adatta alla sinterizzazione.

#### 2.3 Sintesi del Carburo di Tungsteno

Si tratta di una reazione di riduzione carbotermica che avviene in forno, in crogiolo di grafite, di ossido di zirconio o anche allumina fra 1400° e 1600°C in ambiente riducente per presenza di H<sub>2</sub> oppure CO. La presenza di questi gas è opzionale a seconda che si voglia ottenere un prodotto più polverulento oppure più compatto. Questa reazione presenta il vantaggio di riassumere in un solo processo quelle che di solito sono le 2 fasi attraverso le quali si passa e cioè una iniziale riduzione del WO<sub>3</sub> a tungsteno metallico seguita dalla carburazione di quest'ultimo.

La fase di riduzione a tungsteno metallico inizia verso i 650°C ed è totale verso i 1400°C secondo la reazione parziale (3)





Successivamente si ha la sintesi del Carburo con la reazione:



che conclude il processo.

Va osservato che il processo di carburazione dà come prodotto primario il monocarburo WC, come Pirani e Sandor hanno dimostrato, ma nella maggioranza dei casi è presente anche l'emicarburo  $W_2C$ . (1)

### 2.3.1 Riduzione carbotermica

Le miscele essiccate per atomizzazione, liofilizzazione ed evaporazione sono state sottoposte al trattamento di sintesi per l'ottenimento del carburo di tungsteno.

Basandosi sulla reazione fondamentale (a) è stato allestito un programma di prove tale da coprire l'intervallo di temperatura tra 1400 e 1600°C di 50 in 50°C e per tempi di 1 h e 5 h allo scopo di individuare, interpretando i risultati, le condizioni di trattamento più idonee all'ottenimento di un WC ad alto titolo e di granulometria fine. I processi sono stati condotti in un forno tipo Brew 424 C della General Engineering a resistori di tungsteno a rete intrecciata per trattamenti ad alte temperature (sino a 2800°C), in atmosfera riducente.

## 3. CARATTERIZZAZIONE PRODOTTO FINALE

Sui prodotti finali ottenuti sono state condotte caratterizzazioni chimico-fisiche per poter valutare le differenze esistenti tra i vari metodi di preparazione.

Le caratterizzazioni sono state;

- a) Analisi chimica
- b) Analisi strutturale.

- a) Analisi chimica

In figura 2 è riportato il grafico dell'andamento del titolo in WC contenuto nelle polveri in funzione del trattamento termico di sintesi.

Dall'esame di questo grafico si può dedurre quanto segue:

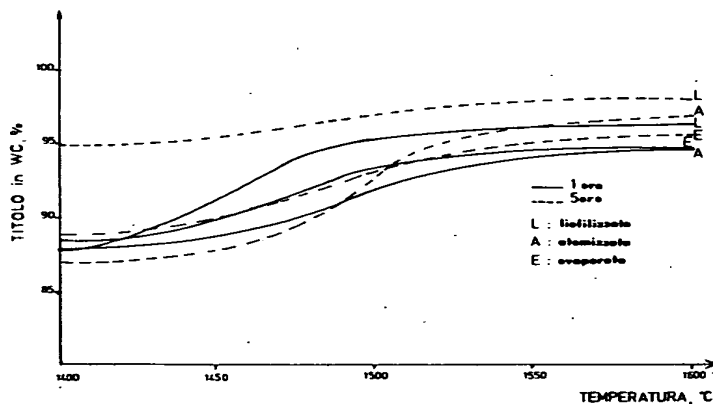


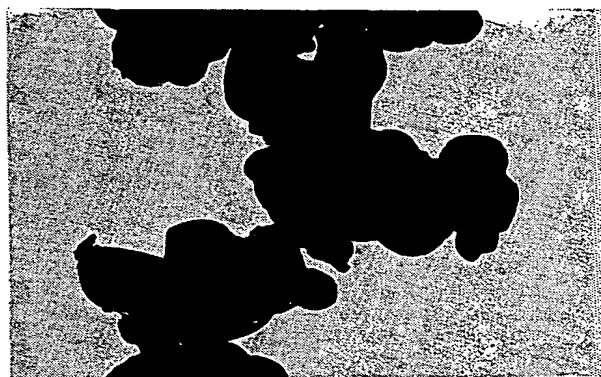
Fig. 2 - Andamento del titolo in WC in funzione del trattamento termico di sintesi

- L'essiccamento per liofilizzazione permette di ottenere, a qualsiasi temperatura il titolo più elevato fino a raggiungere a 1550 e 1600°C il valore massimo del 98%.

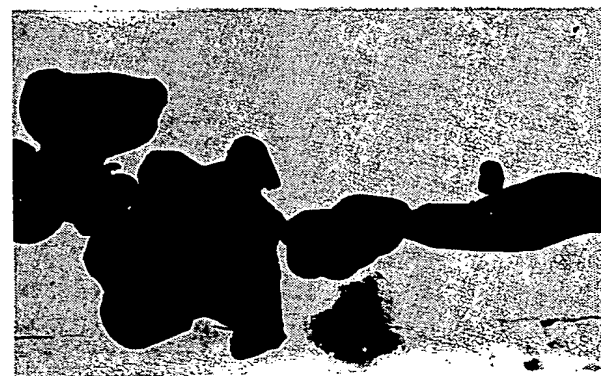
- In tutte le curve si rileva un netto aumento dei valori in prossimità dei 1500°C che ci fa individuare in questo intorno la temperatura minima ottimale.

Il prolungamento nella durata del trattamento favorisce l'incremento del titolo in WC.

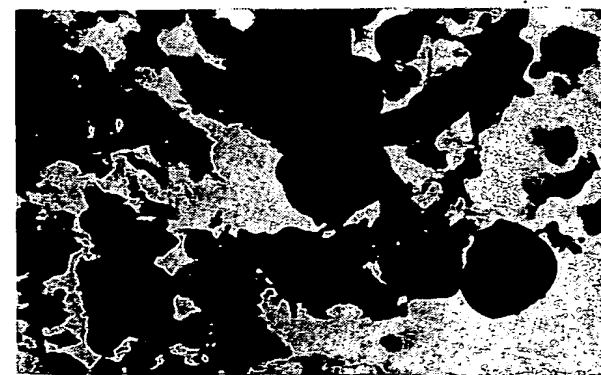
- L'essiccazione per normale evaporazione porta in ogni caso a valori di contenuto in WC più bassi.



a



b



c

Fig. 3 - Aspetto micrografico delle polveri di carburo di tungsteno sintetizzate a 1600°C per 5 ore in  $H_2$ : a) Liofilizzate b) Atomizzate c) Evaporate (5000 x)

### b) Analisi strutturale

L'evoluzione strutturale delle polveri di Carburo di Tungsteno in funzione del tipo di essiccamento delle polveri di partenza e del trattamento termico di sintesi è stata seguita mediante diffrazione a raggi X (diffrattometro Philips PM 1310) e mediante microscopia ottica ed elettronica.

I composti e le fasi cristalline presenti nelle polveri ottenute sono riportate in tab. 3. Esaminando i dati riportati si nota la presenza in alcuni campioni dell'emicarburo di tungsteno ( $W_2C$ ); in particolare a bassa temperatura e negli evaporati normalmente, la presenza di questo composto, che è da considerarsi negativa a causa di una sua minore resistenza agli acidi rispetto al WC, appare sensibile. I campioni atomizzati e liofilizzati risultano ancora qualitativamente i migliori, in particolare dopo il trattamento a  $1600^\circ C$ : infatti sono praticamente costituiti solo da WC. Le microscopie elettroniche riportate in fig. 3 confermano la qualità superiore delle polveri atomizzate e liofilizzate rispetto a quelle evaporate normalmente.

Queste micrografie rappresentano le polveri ottenute con il trattamento a  $1600^\circ C$  per 5 ore che ha dato in tutti e tre i casi il titolo più elevato in Carburo di Tungsteno.

Risulta evidente come la polvere liofilizzata (fig. 3a), oltre ad avere il titolo più alto in assoluto, appare totalmente monofasica, senza cioè  $W_2C$  e carbonio grafítico; carbonio che è presente invece in tracce nell'atomizzata (fig. 3b) e in larga misura nella evaporata normalmente (fig. 3c).

In fig. 4 infine sono riportate le microscopie ottiche delle stesse polveri, dove è possibile rilevarne le granulometria media.

La granulometria media della polvere di WC ottenuta per evaporazione normale appare nettamente maggiore di quelle ottenute per atomizzazione e liofilizzazione; infatti il grano medio è dell'ordine di  $2,5 \div 3 \mu$ , che è granulometria di tipo commerciale (fig. 4c), mentre le altre due hanno una dimensione media dell'ordine di  $1 \mu$ , con numerose punte al di sotto del micron (fig. 4a e 4b).

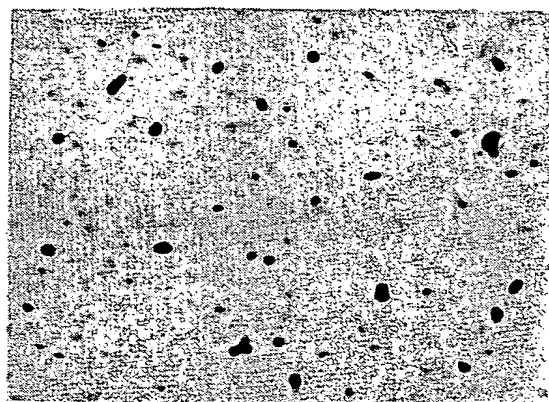
Risulta quindi evidente, sotto tutti gli aspetti, che l'introduzione, di tecniche di essiccamento come la liofilizzazione e l'atomizzazione favorisce l'ottenimento di un prodotto qualitativamente superiore. Questo avviene soprattutto perchè, potendo impiegare soluzioni o sospensioni dei prodotti di partenza, si realizza una miscelazione talmente intima ed omogenea da rendere macroscopici i vantaggi che se ne possono trarre.

### 4. CONCLUSIONI

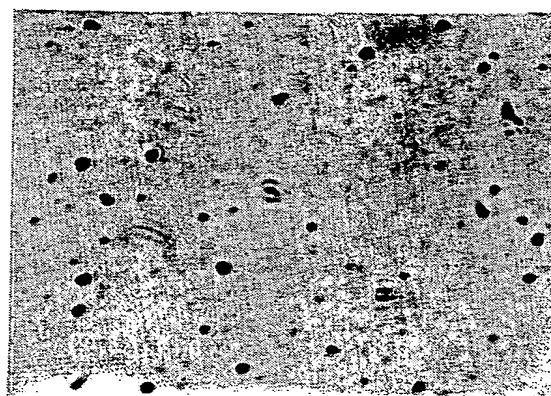
In base ai risultati delle caratterizzazioni sopraelletuate è possibile concludere:

- L'essiccamento per atomizzazione e liofilizzazione e particolarmente indicato per questo tipo di preparazione in quanto impiegando soluzioni o sospensioni è possibile realizzare una miscelazione dei prodotti di partenza eccellente.

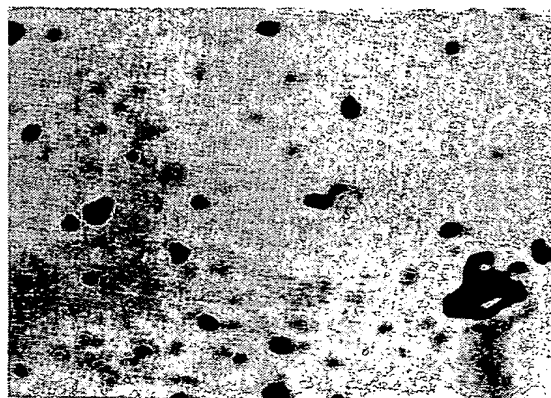
- La reazione di sintesi del Carburo di Tungsteno può essere effettuata con un unico trattamento termico,



a)  $\bar{\phi} = 1 \mu$



b)  $\bar{\phi} = 0,5 \div 1 \mu$



c)  $\bar{\phi} = 2,5 \div 3 \mu$

Fig. 4 - Dimensione media dei granuli delle polveri di Carburo di Tungsteno sintetizzato a  $1600^\circ C$  per 5 h in  $H_2$ : a) Liofilizzata b) Atomizzata c) Evaporata (1000 x)

che a partire da  $1500^\circ C$  e per tempi di alcune ore (5) permette di ottenere titoli in Carburo fino al 98%.

- L'essiccamento per atomizzazione e liofilizzazione infine, permette di ottenere polveri di Carburo di Tungsteno a granulometria più fine (diametro medio  $1 \mu$ ) e più omogenea delle polveri che si possono ottenere con altri metodi di essiccamento.

- Il prodotto ottenibile con queste tecniche di preparazione quindi, presenta caratteristiche chimico-fisiche tali da renderlo specialmente adatto alla realizzazione di particolari sinterizzati in Carburo di Tungsteno di qualità superiore.

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